



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08J 9/32, B29C 67/20, F16L 59/02	A1	(11) International Publication Number: WO 99/57182 (43) International Publication Date: 11 November 1999 (11.11.99)
(21) International Application Number: PCT/US99/09401 (22) International Filing Date: 30 April 1999 (30.04.99) (30) Priority Data: 60/083,888 1 May 1998 (01.05.98) US 60/083,885 1 May 1998 (01.05.98) US (71) Applicant: TEXTRON SYSTEMS CORPORATION [US/US]; 201 Lowell Street, Wilmington, MA 01887-2941 (US). (72) Inventors: BERTRAND, David, C.; 203 Kinsley Street, Nashua, NH 03060 (US). CASTLE, George, K.; 56 Pierce Lane, Hollis, NH 03049 (US). HANAFIN, Joseph, W.; 44 Kelleher Street, Marlborough, MA 01752 (US). (74) Agents: PIERCE, N., Scott et al.; Hamilton, Brook, Smith & Reynolds, P.C., Two Militia Drive, Lexington, MA 02421 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: EPOXY-SYNTACTIC-FOAM-INSULATED METAL PIPES		
(57) Abstract A lightweight, insulated pipe for underwater or out of water use, including a metal pipe and an insulation layer covering the metal pipe, wherein the insulation layer includes at least one cured epoxy resin binder and hollow microballoons. The pipe is formed on a metal pipe by first forming a liquid epoxy-based mastic comprising at least one type of epoxy resin and having microballoons dispersed therein. The liquid mastic is then applied onto the exterior surface of a metal pipe to form a mastic coating on that surface. The mastic coating is then allowed to cure, or is cured to form a low density syntactic foam insulation layer.		

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EPOXY-SYNTACTIC-FOAM-INSULATED METAL PIPES

BACKGROUND OF THE INVENTION

Undersea pipelines often require thermal insulation to reduce heat transfer between the contents of the pipe and the surrounding water. This is done, for
5 example, when conveying high-wax-content crude petroleum to prevent deposit of waxes or gas hydrates on the pipeline walls, which will, in turn, restrict petroleum flow.

However, current methods of insulating undersea pipelines may not be suitable at lower depths, such as 6000 to 7000 feet (about 1.8 km to about 2.1 km),
10 because (1) unprotected insulation materials often compress due to the high water pressure, thereby degrading its insulative properties, and (2) the use of a metal outer pipe, surrounding the inner pipe and insulation, for deep water applications is not suitable due to its sheer weight and inflexibility and the difficulty of fabricating a pipe-laying tender.

15 Therefore, a need exists for lighter weight, easily formed, insulated metal pipe whose insulation will not be crushed at deep water pressures.

SUMMARY OF THE INVENTION

This invention relates to insulated metal pipe and methods of forming said pipe. Embodiments of the insulated metal pipes of this invention are suitable both
20 for underwater use and for use out of water.

The insulated pipe includes a metal pipe coated with a primer layer and an insulation layer covering the primer layer, wherein the insulation layer includes at least one cured epoxy resin binder and hollow microballoons.

In methods of this invention, a syntactic foam insulation layer is formed on a
25 metal pipe by first forming a liquid epoxy-based mastic comprising at least one type of epoxy resin and microballoons dispersed therein. The liquid mastic is then

applied onto the exterior surface of the metal pipe to form a mastic coating on that surface. The mastic coating is then allowed to cure, or is cured, to form a syntactic foam insulation layer.

Preferred embodiments of this invention offer the advantage that the syntactic foam insulation of the insulated pipe is light weight, is crush-resistant at deep submergence depths, is easily applied to the welded joints of the metal pipeline sections on the pipe-laying tender just before being laid underwater, and is sufficiently flexible to be laid to form an underwater pipeline.

Another advantage found in preferred embodiments of the invention is that the mastic used to form the syntactic foam insulation includes high-crush strength microballoons that can withstand the pressures or sheer forces generated when the mastic is applied using commercial spray equipment or when the mastic is manufactured using commercially-available medium-to-high sheer processing equipment, thereby facilitating the use of such equipment in forming the syntactic foam insulation.

Further, when used in non-submerged applications, syntactic foam insulation of this invention offers the advantages of being light weight and providing corrosion resistance to corrosion-susceptible pipes.

DETAILED DESCRIPTION OF THE INVENTION

The term, "metal pipes," is defined herein to include metal pipes, pipe joints, flanges, pipelines, tubes, vessels, reactors, tanks and other systems and components which internally transmit or store gases or fluids, which can experience significant heat transfer across the pipe wall between the pipe interior and the exterior environment.

Typically, the metal pipes of the present invention have exterior surfaces that are at least partially susceptible to corrosion. Further, metal pipes of the present invention typically have contact surface temperatures of about 250°F, or less, at the exterior surfaces, due to the flow of heated fluids and or gases through the metal pipe. Alternatively, the fluid or gas flowing through the pipe is at a temperature below ambient.

The term, "crush-resistant," is defined herein as the ability to withstand prolonged exposure to the pressures associated with deep underwater submergence, such as at depths of about 6000 feet (about 1.8 km) or more, without significant physical degradation or loss of insulative properties.

- 5 A composite insulation layer, suitable for the present invention, comprises a cured epoxy thermoset binder containing a substantially homogeneous dispersion of at least one type of hollow microballoon or hollow microsphere (hereinafter, "microballoons").

Suitable liquid epoxy resins used to form the cured binder include aliphatic,
10 aromatic, cyclic, acyclic, alicyclic and heterocyclic epoxy resins or blends thereof. For instance, examples of suitable epoxy resins include glycidyl ethers derived from such polyhydric alcohols as ethylene glycol; diethylene glycol; triethylene glycol, 1,2-propylene glycol; 1,4-butylene glycol; 1,5-pentanediol; 1,2,6-hexanetriol; glycerol; trimethylolpropane; neopentyl glycol; Bisphenol-A (a condensation
15 product of phenol and acetone) and Bisphenol-F (a condensation product of phenol and formaldehyde). Other suitable epoxy resins include di-epoxides such as the reaction product of epichlorohydrin and a polyglycol (Dow D.E.R.[®] 736 or D.E.R.[®] 732) or the reaction product of epichlorohydrin and neopentyl glycol (Air Products Epodil[®] 749).

- 20 A preferred epoxy resin is (2,2-bis[4-(2'3'-epoxy propoxy)phenyl] propane, commonly called the diglycidyl ether of bisphenol A (DGEBA) (e.g., Shell EPON[®] Resin 825, Shell EPON[®] 828, Dow D.E.R.[®] 331 or Dow D.E.R.[®] 332).

The epoxy resin of the present invention can also include blends of different epoxy resins, for instance a blend of DGEBA and an aliphatic glycidyl ether (e.g.,
25 Dow D.E.R.[®] 324) or, more preferably, a blend of a DGEBA resin (e.g., Dow D.E.R.[®] 331) with a low viscosity difunctional epoxy resin (e.g., Air Products Epodil[®] 749) which is believed to improve the flexibility of the composite insulation and lower the viscosity to allow increased loading of microballoons.

Microballoons suitable for incorporation in the composite insulation layer of
30 this invention, are nonporous microspheres and microballoons which are generally impermeable to water and to epoxy resin, and which lower the density and reduce the thermal conductivity of the insulation layer. Suitable microballons are typically

spherical in shape. Examples of suitable microballoons include, for instance, ceramic, organic and/or glass microballoons (e.g., SCOTCHLITE S38 glass bubbles from 3M Corporation, St. Paul, Minnesota).

5 Preferably, the microballoons that are mixed with the epoxy binder generally will not break, fracture or collapse during processing with medium to high shear processing equipment. In a "medium to high shear" mixer, for example, the speed of the mixing blade is greater than 3000 ft/min. (15 m/s). Preferably the crush strength of the microballoons is at least 4000 pounds per square inch (28 MPa).

10 Further, preferred microballoons generally also will not break, fracture or collapse during application of the epoxy mastic, such as during pumping and spraying, to form an insulation layer.

Further still, the microballoons should be strong enough to be able to withstand pressures of up to about 42 pounds per square inch (psi) (290kPa) or more per 100 feet of depth for the desired pipe depths at which the insulation is to be used.
15 More preferably, the microballons can withstand water pressures of about 4200 psi (29 MPa) or more, which corresponds to a water depth of about 10,000 feet. However, the microballoons should be sufficiently low in density that the thermal conductivity of the insulation layer is not significantly increased.

The weight ratio of microballoons to cured epoxy (consisting essentially of epoxy resin plus curing agent) in the composite layer is usually between about 1:5 to about 1:1, and is preferably between about 1:3 to about 1:1.
20

Typically, the microballoons have a particle size (diameter) between about 5 to about 500 micrometers (microns). Preferably, the microballoons should be small enough in size to be freely sprayable, typically about 125 microns, or less. More
25 preferably, the microballoon particle size is between about 8 and about 150 microns.

Optionally, the insulation layer of the present invention further includes a dispersion of one or more types of milled, flaked or chopped fibers. Typical fibers are formed, for example, of glass, carbon or ceramic. Preferably, the fibers are formed of glass.

30 Fibers may be added (1) to reinforce the cured composite insulation layer and prevent fracture thereof under high pressures, (2) as anti-separation agents for

the liquid mastic, or portions thereof, and (3) to improve the water resistance of the insulation layer.

The weight ratio of fiber-to-epoxy in the composite insulation layer is usually between about 1:300 to about 1:30.

5 Fibers, used in the method and composition of this invention, should have a length and width sufficient to enhance the mechanical properties of the composite insulation layer. Typically, fibers used herein are between about 1/32 inches to about 1/8 inches, or more, in length. Further, fibers of the present invention are typically between about 5 to about 25 microns, or more, in diameter, and preferably
10 about 16 microns.

In the mode wherein the composite mastic is applied by spraying, it is preferred the fiber length be sufficiently small to pass through the spray nozzle without significant clogging, typically a length of about 1/8 inches, or less.

In a specific embodiment, the composite insulation layer further includes
15 minute particles of amorphous silica, which are dispersed in the mastic. The amorphous silica is added to improve thixotropy and to prevent significant separation of fillers. Examples of suitable minute amorphous silica particles include flame silica, arc silica, precipitated silica and fumed silica. Preferably, the amorphous silica is hydrophobic fumed silica and/or hydrophilic fumed silica. More
20 preferably, the fumed silica is a surface-treated silica, for instance a silica treated with dimethyldichlorosilane or hexamethyldisilazane. Most preferably, the amorphous silica particles are polydimethylsiloxane oil-treated fumed silica particles.

Preferably, the composite insulation layer has a ratio of silica particles to
25 epoxy between about 1:200 to about 1:10.

More preferably, the amorphous silica particles have a surface area between about 50 and 500 m²/g and a particle size between about 3 to about 50 nanometers.

In some embodiments of the present invention, the metal pipe contains more than one insulation layer. The inner insulation layer has a lower density than the
30 outer insulation layer due to the inner layer containing gas bubbles dispersed therein. The method of forming an insulation layer of lower density, by dispersing air bubbles therein, is described in copending U.S. Provisional Patent Application No.

60/083,888, "Corrosion Resistant, Epoxy Syntactic Foam Insulated Pipe", Attorney Docket No. TSC96-02P, filed on May 1, 1998.

5 A preferred formulation of the composite insulation layer comprises between about 40 to about 89.5 grams of cured epoxy binder, about 10 to about 50 grams of glass microballoons, 0 to about 1 gram of glass fiber, and about 0.25 to about 5.0 grams of fumed silica particles, wherein the sum total weight of the formulation is about 100 grams.

10 The mastic used to form the composite insulation layer of the present invention comprises at least one suitable liquid epoxy resin, at least one curing agent and at least one liquid reactive diluent, in addition to the fillers described above.

Typically, any curing agents used to harden the epoxy resins described herein can be used within the mastic to form the cured epoxy binder. The curing agent reacts with the epoxy resin to cross-link the resin and form a hard, durable material. Examples of suitable curing agents can include, for instance,
15 cycloaliphatic amine (ANCAMINE® 2167), diethylenetriamine (ANCAMINE® T), 3, 3-amino bis propylamine, triethylenetetraamine (ANCAMINE® 1769), cyanoguanidine, tetraethylene pentamine, m-xylenediamine, di-carboxylic acids, tri-carboxylic acids, oxalic acid, phthalic acid, terephthalic acid, succinic acid, substituted succinic acids, tartaric acid, polymerized fatty acids, pyromellitic
20 anhydride, maleic anhydride, or combinations thereof. The preferred curing agent is an amidoamine (Ancamide® 903 MAV from Air Products).

Liquid reactive diluents are used to lower the viscosity of the composite mastic. Diluents suitable for the present invention include mono-functional glycidyl ethers, di-functional glycidyl ethers or combinations thereof. The preferred liquid
25 reactive diluent is an aliphatic diglycidyl ether (Epodil® 749).

A suitable formulation of the composite mastic of the present invention would include between about 30 to about 50 grams of liquid epoxy resin, between 0 to about 15 grams of liquid reactive diluent, and between about 5 to about 50 grams of total curing agent.

Additional components can be added to the mastic to ease formulation of the mastic, such as wetting agents and anti-foaming agents. Further, the mastic, or portions thereof, may be pigmented such as for identification purposes.

In a preferred composite mastic formulation, wherein the mastic is formed from two separate components just prior to curing, the mastic includes between about 25 - 50 grams total of liquid epoxy resins, 5 - 46 grams of curing agent, 0 - 7 grams of liquid reactive diluent, 10 - 50 grams of glass microballoons, 0 - 1 grams of glass fiber and 0 - 5.0 grams of fumed silica particles.

In a more preferred composite mastic, wherein the mastic is formed from two separate components just prior to curing, the mastic includes between about 28.0 - 36.0 grams of DGEBA, about 3.6 - 6.0 grams of low viscosity difunctional epoxy resin (e.g., Epodil® 749), 20.9 - 25.9 grams of curing agent, and 31 - 42 grams of glass microballoons.

Alternatively, a preferred single-component formulation of the composite mastic includes between about 50 - 75 grams of liquid epoxy resin, 5 - 15 grams of heat activated curing agent such as cyanoguanidine, 1 - 4 grams of curing accelerator, such as imidazole, 0 - 10 grams of liquid reactive diluent, 10 - 50 grams of glass microballoons, 0 - 1 grams of glass fiber and 0 - 3.0 grams of fumed silica particles.

In applications where greater flexibility is required (for example, in the laying of deep-sea pipelines), the liquid epoxy resin and/or curing agent can be replaced, at levels from 20% to 50% by weight, with suitable flexibilizing agents. Preferably, the flexibilizing agents are 100% reactive resins. Examples of suitable epoxy resin side flexibilizers include epoxy-modified urethane (available as GVI-4029 from Pacific Epoxy Polymer (PEP)); castor oil triglycidyl ether (available as PEP-6755 from Pacific Epoxy Polymer); dimer fatty acid diglycidyl ester (available as HELOXY Modifier 71 from Shell Chemical Co.); polypropyleneglycol glycidyl ether/epoxy blend (available as ARALDITE GY 508 from CVC Specialty Chemicals); and elastomer-modified epoxy (available as EMRM-20 from CVC Specialty Chemicals). Examples of suitable curing agent side flexibilizers include modified aliphatic amine (available as ANCAMINE 2390 from Air Products);

polyoxypropylenediamines (available as JEFFAMINE D-400 and D-2000 from Huntsman Petrochemical.

Mastic formulations that include flexibilizers typically exhibit increases in flexibility (as determined by total strain per ASTM D-638) fo 100% to 500% over formulations without flexibilizers.

The table, below, provides a comparison of preferred compositions of first and second components of composite mastic with a flexibilizing agent ("Flexibilized") and without a flexibilizing agent ("Unflexibilized"). In each "flexibilized" formulation, the flexibilizing agent replaces 50% of the liquid epoxy or curing agent, relative to the "unflexibilized" formulation.

Ingredients	Unflexibilized: 1st Component weight %	Flexibilized: 1st Component weight %	Unflexibilized: 2nd Component weight %	Flexibilized 2ndComponent weight %
Epoxy resin (DER 331)	52.59	30.295	-	-
Epoxy resin side flexibilizer	-	30.295	-	-
Epoxy diluent (Epodil 749)	8.00	-	-	-
Curing agent (Ancamide 903MAV)	-	-	59.79	29.895
Curing agent side flexibilizer	-	-	-	29.895
Yellow pigment	1.00	1.00	-	-
White pigment	-	-	0.20	0.20
Wetting agent (BYK W-990)	0.40	0.40	0.40	0.40
Antifoam agent (Sag 47)	0.010	0.010	0.010	0.010
Hydrophilic fumed silica	-	-	1.55	1.55
Hydrophobic fumed silica	2.00	2.00	-	-
Glass bubbles (3M S38 bubbles)	36.00	36.00	38.05	38.05
Total	100.00	100.00	100.00	100.00

Note: flexibilized formulations shown above are at 50% flexibilizer replacing liquid epoxy/curing agent.

In additional embodiments, the insulated metal pipe of the present invention further includes a water-resistant primer layer disposed between the metal pipe and

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the composite insulation layer. Such a primer layer comprises a hydrophobic or water-resistant material that will remain bonded to the metal pipe and bonded to the epoxy-based insulation layer at pipe contact temperatures of up to about 250°F. This primer layer is formed by applying a suitable primer to the exterior surfaces of the metal pipe to be protected. Examples of suitable primers include, for instance, anti-corrosion epoxy-based or zinc-based primers such as are known in the art, for instance bisphenol epoxy polyamides, epoxy aluminum surface tolerant (e.g., HEMPADUR 4515 from Hempel, west blast primers epoxy (e.g., 2 TW 500 from Azko Nobel), zinc rich epoxies (e.g. AMERCOAT 68 from Ameron), zinc rich epoxies containing an epoxy tie coat (e.g., AMERCOAT 68/AMERCOAT 71 from Ameron), inorganic zinc silicates with an epoxy tie coat (e.g., DIEMETCOTE 9/AMERCOAT 71 from Ameron), inorganic ceramic silicates (INTERPLATE NIPPE CERAMO from International Paint), and zinc phosphate (e.g., INTERGARD 251 from International Paint).

15 The primer coat is applied to the metal part by any known primer application means, such as by painting, spraying, dipping or extrusion. The typical primer layer thickness is between about 0.5 to about 5.0 mils.

In yet another embodiment, such as where the insulation layer is pre-cast and cured and then attached to the metal pipe, the metal pipe of the present invention further includes an adhesive layer disposed adjacent to the inner surface of the composite insulation layer. Adhesives suitable to the present invention are those that will bond to a metal pipe, or a primer layer, and to the epoxy syntactic foam insulation layer at temperatures of up to 250°F, such as Araldite® 2011 Multipurpose viscous adhesive (from Ciba), Araldite® 2014 Heat/Chemical-Resistant two-component paste adhesive (from Ciba) and XMH 8574 Resin/Hardener two-part epoxy adhesive (from Ciba).

25 The adhesive layer is applied to the metal part, or to the primer layer if the metal is primed, or to the interior surface of the pre-cast insulation, by any known adhesive application means, such as by painting, spraying, dipping or extruding.

30 In one embodiment of the method for forming an insulated metal pipe, the insulation layer is formed on the exterior surface of the pipe by applying the composite mastic, in a liquid state, such as by trowelling, spraying or extruding, to

the exterior surface of the pipe, or optional primer layer, and then curing the mastic in place.

Alternatively, an insulated metal pipe for undersea use is formed by bonding or fixing a pre-formed, cured composite insulation around the metal pipe. The
5 composite insulation is formed from a composite mastic that has been molded into the desired shape or form and that can be cured under ambient conditions by heating, or irradiating the mastic.

The two components of the composite mastic of the present invention are mixed together prior to curing. Mixing is performed by one or more means suitable
10 to form a substantially-homogeneous mixture of the mastic components (e.g., liquid epoxy resins, curing agent, liquid diluent, particulates and fibers). Suitable means for mixing without causing significant damage to the hollow microballoons include a high-speed dispersion mixer, a Hobart mixer, a static mixer, or a combination of different shear mixers. Typically, the microballoons are mixed into the mastic, or
15 into components thereof, under low-shear mixing conditions, however, high-shear mixing means can be employed when mixing high strength microballoons.

It is preferred that the mastic be formed from two separate components, a first component that contains the epoxy resin and a second component that contains at least one ambient-temperature curing agent.

20 It is also preferred that the epoxy resin and the ambient-temperature curing agent, or the components containing the same, be mixed immediately prior to or during application, such as by flow through a static mixer, prior to being applied.

The cured insulation layer is then formed on the exterior of the metal pipe or optional primer layer. The composite layer can be formed (a) by attaching
25 previously molded pieces of cured composite insulation to the pipe which were fabricated by curing the composite mastic within a mold or while molded around a section of similar pipe, (b) by spraying, dispensing or extruding the composite mastic on the metal pipe and then curing the mastic in place, or (c) by trowelling the mastic onto the metal pipe and then curing in place.

30 Where the composite insulation layer is formed from molded pieces, these pieces are typically attached to the primer layer by using a suitable adhesive, which

is applied to the primer layer and/or to the inside surface on the molded piece. Typically, a layer of about 1/4 to 1 mm of adhesive is used.

The use of pre-molded insulation pieces is preferred wherein the metal pipe is operating at elevated temperatures during application of the insulation layer.

- 5 However, the mastic can be applied to elevated-temperature pipes, components and systems by trowelling or spraying.

- However, it is more preferred that the cured composite insulation layer be formed on the pipe while the pipe is at normal ambient temperatures. The preferred method of applying the mastic to the primer layer is by spraying droplets, more preferably in a fan-shaped spray pattern, which are directed towards the surface to be coated. Suitable droplet size can be formed by directing mastic through a nozzle with a diamond-shaped spray tip of an inner diameter typically between about 33 and about 47 thousandths of an inch. Other means for forming equivalent-sized droplets, as are known in the art, are also suitable for the method of this invention.
- 10 Typically, the mastic is pressurized to between about 1000 psi and about 4000 psi.

It is additionally preferred that the mastic components, such as are in a two-component system, be heated to reduce their viscosity and enhance ease of application. Typically, the mastic components are heated to between about 40°C and about 75°C.

- 20 The spray is then usually directed, but not required to be directed, in a back and forth motion across the surfaces to be coated until a suitable thickness of low density mastic coating is deposited on the surface. Typically, about 25 mm or less (preferably about 10 mm to about 20 mm) of mastic is applied in a single coating. Repeated coatings can be applied to attain the desired coating thickness. Preferably,
- 25 second coatings are not be applied until the first coating has set or at least partially cured, typically about 30 minutes to 4 hours after application of the first coating.

- Where the insulated pipe is to be used for non-submerged (rather than underwater) applications, it is preferred that at least one gas be dispersed within the mastic, or at least one of its components, prior to applying the mastic. For example,
- 30 where the mastic is applied by spraying, the components of the mastic can be contained in separate tanks. The components of the mastic are then heated and stirred, such as with a paddle or other suitable stirrer, while the tanks are pressurized

with a gas (e.g., air), typically to a pressure between about 40 psi to about 100 psi, to disperse additional gas into the mastic components.

Specifically, the gas can be added directly into the mastic and/or to one or more of its separate components (e.g., the mastic components described in Examples 1 and 2). One suitable means to add gas to the mastic is by stirring each component of the mastic within a gas pressurized container just before applying the mastic, such as by the method described in Example 3. Preferably, the gas is added to the mastic, or to a component of the mastic, just prior to application.

The more gas dispersed into the mastic, typically by stirring while gas pressurized, the lower the density of the final composite insulation.

The use of mastic application methods, that do not introduce air into the mastic prior to application, will typically result in higher densities for the composite insulation layer than would be achieved through applying the mastic after dispersing gas therein.

After application of the composite mastic to the primer layer, the mastic is allowed to cure in air.

In additional embodiments of the method of the present invention for forming a corrosion-resistant, epoxy syntactic foam insulated metal pipe, the metal pipe is first prepared so that a primer layer can adhere to it, such as by removing rust, scale and other contaminants, typically by blasting or chemical treating the outside pipe surface.

After preparation of the surface of the metal pipe, the primer layer is then applied to form a coating having a thickness suitable to completely cover the surface of the pipe without trapping significant amounts of solvent within the primer layer as the primer cures. Typically, the primer layer is between about 2 mils to about 5 mils thick.

In another optional embodiment of the method of the present invention, a paint, coating, film covering or other protective layer can be applied to the cured composite insulation layer formed on the metal pipe to further protect the insulation layer from mechanical damage, aging or degradation due to environmental exposure such as from salt water immersion.

The invention will now be further and specifically described by the following examples.

EXAMPLE 1: Preparation of a First Component of Ingredients for Forming an Epoxy Syntactic Foam Composite Mastic

5 One hundred pounds of a first component used in forming the epoxy syntactic foam composite mastic of the present invention, was prepared as follows:

 DGEBA (53.4 lbs. of D.E.R.[®] 331 purchased from Dow Chemical U.S.A., Midland, Michigan) was warmed to between 110°F and 120°F. Then, into a mixing kettle were added the warmed DGEBA, neopentyl glycol diglycidyl ether (8.0 lbs. of

10 EPODIL[®] 749 liquid reactive diluent, purchased from Air Products and Chemicals, Inc., Allentown, Pennsylvania), black pigment (0.2 lbs of VN-6792 purchased from Ferro Corporation, Edison, New Jersey), wetting agent (0.4 lbs of BYK[®] W990, a partial salt of acidic polyesters, purchased from BYK Chemie, Wallingford, Connecticut), and 0.01 lbs of SAG 47 polydimethylsiloxane (modified) anti-foaming

15 surfactant (purchased from OSi Specialties, Inc., Danbury, Connecticut). The contents of the mixing kettle were then mixed at 750 rpm for 15 minutes by a HOCKMEYER 550L high-speed dispersion mixer with a G-style blade (Hockmeyer Equipment Corp., Harrison, New Jersey).

 While continuing to mix at 750 rpm, 2.0 lbs of CAB-O-SIL[®] TS-720

20 amorphous hydrophobic fumed silica (purchased from Cabot Corporation, Tuscola, Illinois) was gradually added to the mixing vortex. After the fumed silica was observably wetted, mixing speed was increased to 1100 rpm, after which mixing continued for at least 15 minutes until the fumed silica was sufficiently dispersed to a Hegman Grind between 4 and 7.5 as measured using a Hegman Grind Gauge

25 (purchased from Precision Gage & Tool Co., Dayton, OH). Hegman Grind measurements are described in "Reading the Hegman Grind Gauge," PAINT, OIL & CHEMICAL REVIEW (June 22, 1950).

 Mixing speed was then lowered to 550 rpm and hollow glass microballoons (36 lbs of SCOTCHLITE S-38 from 3M Corporation, St. Paul, Minnesota) were

added to the mixing kettle. After completing the addition, the contents of the mixing kettle were then mixed for an additional 10 minutes at 750 rpm.

The viscosity of the first component in the mixing kettle was then determined at 49°C and 1 rpm using a Brookfield viscometer (Model RVT-DV1) with a T-spindle. A suitable viscosity for the first component was between about 500,000 to about 1.5 million centipoise.

During the production of the first component, the mixing blade height may have to be adjusted to maintain a vortex while mixing. Also, throughout the production of the first component, temperature of the mixture in the mixing kettle was maintained at or below 60°C.

The first component was then packaged in 6 gallon pails.

EXAMPLE 2: Preparation of a Second Component of Ingredients for Forming an Epoxy Syntactic Foam Composite Mastic

One hundred pounds of a second component of the ingredients used in forming an epoxy syntactic foam composite mastic of the present invention, was prepared as follows:

A polyamidoamine curing agent (59.7 lbs of 903 MAV), 0.2 lbs of white pigment (48-18000 from Ferro Corporation), wetting agent (0.4 lbs of BYK® - W990 from BYK Chemie, Wallingford, CT) and anti-foaming surfactant (0.01 lbs of SAG 47) were added to a mixing kettle while mixing at 500 rpm, by a high speed dispersion mixer (HOCKMEYER 550L with a G-style blade) for 15 minutes.

Mixing speed was then raised to 750 rpm and then 1.55 lbs of amorphous hydrophilic silicon dioxide fumed silica (CAB-0-SIL® M-5 fumed silica, purchased from Cabot Corporation) was gradually added to the mixing vortex. After the fumed silica was wetted in, mixing speed was raised to 1000 rpm, after which mixing continued for at least 15 minutes until the fumed silica was sufficiently dispersed to a Hegman Grind between 4-7.5 as measured using a Hegman Grind Gauge.

The mixing speed was then reduced to 550 rpm and hollow glass microballoons (38.1 lbs of SCOTCHLITE S-38) were added to the mixing kettle.

After completing the addition, the mixing speed was raised to 700 rpm for 15 minutes.

The viscosity of the second component in the mixing kettle was then determined at 49°C and 1 rpm using a Brookfield Viscometer (Model RVT-DV1) with a T-spindle. A suitable viscosity for the second component was between about 500,000 to about 1.5 million centipoise.

During the production of the second component, the mixing blade height may have to be adjusted to maintain a vortex while mixing. Also, throughout the production of the second component, temperature of the mixture in the mixing kettle was maintained at or below 60°C to prevent polymerization of the epoxy resin.

The second component was then stored in 6 gallon pails.

EXAMPLE 3: Low-Density Composite Insulation

A composite mastic coating, suitable for above-ground use, was applied to various substrates by mixing the first component and the second component using a plural component spray machine (AirTech, Houston, Texas). The spray machine heated and pumped each component from separate holding tanks through one in-line 12-inch static mixer and then discharged a fan-shaped mastic spray through a diamond-shaped spray tipped nozzle (.035-inch inner diameter, Graco, Minneapolis, MN).

The spray machine heated the components to temperatures between about 54°C and about 70°C to reduce the viscosity of the components and promote better mixing of the components and ease of spraying. Prior to and during spraying, the separate components contained in each holding tank are stirred slowly with a scraper type mixing blade. The holding tanks were pressurized with air to between about 60 and about 50 psi, respectively, for the first component and the second component. For undersea applications, the holding tanks preferably would not be pressurized so as to prevent the formation of air bubbles in the mastic.

The spray machine also pressurized the mastic entering the nozzle to a pressure between about 2000 psi to 3000 psi.

This spray machine mixed a mastic containing about 60% of the first component and about 40% of the second component.

The spray was then directed in a back and forth motion across the surfaces to be coated until a 4-mm to 6-mm thickness of low density mastic coating was deposited on the surface. Repeated coatings were applied, as necessary, to attain the desired coating thickness. The second coatings were not applied until the prior coating had gelled.

EXAMPLE 4: Service Temperature Tests

Testing was performed in accordance with ASTM C 447-85, "Standard Practice for Estimating the Maximum Use Temperature of Thermal Insulations", on six ten-foot samples of an epoxy syntactic foam of the present invention. The foam was applied to a metal pipe through which oil, at a temperature of 250°F, was circulated.

The purpose of this test was to determine the short-term and long-term service temperature of the epoxy syntactic foam insulation. The service temperatures are those temperatures that the insulation could experience without significant degradation thereby resulting in the loss of thermal insulation capacity.

The test results, after continuously testing for 12 months, showed no loss of thermal insulation capacity.

EXAMPLE 5: Thermal Expansion Tests

The coefficient of thermal expansion was determined for an epoxy syntactic foam of the present invention between various temperatures. The testing was performed in accordance with ASTM E 228-95, "Standard Test Method for Linear Thermal Expansion of Solid Materials With a Vitreous Silica Dilatometer." The purpose of this test was to determine if the coefficient of thermal expansion would be consistent with the use of insulating metal pipes. Two samples of syntactic foam insulation of this invention were tested at each temperature range.

The measured coefficients of thermal expansion were found to be 32.4×10^{-6} cm/cm between -46°C and 21°C , and 45.0×10^{-6} cm/cm between 21°C and 127°C which is suitable for insulating metal pipes.

EXAMPLE 6: Tensile Strength Tests

5 Tensile strength testing was performed in accordance with ASTM D638-96, "Standard Test Method for Tensile Properties of Plastics." Five samples of an epoxy syntactic foam of the present invention were tested.

The test results found that the average tensile strength of this foam insulation was 12.8 MPa.

10 EXAMPLE 7: Impact Strength Tests

Impact strength testing was performed on samples of an epoxy syntactic foam of the present invention. A 2-inch thick layer of foam insulation was applied to a pipe with a 1.875-inch outer diameter by casting pieces of insulation and then adhesively fixing those pieces to the pipe. The weight of the pipe was supported by
15 a 1-1/4-inch steel support rod during the test.

In the test, force was applied at the seam line and 90 degrees from the seam line of the insulation on the pipe by impacting the pipe with a 1/2-inch indenter with various levels of force at various pipe temperatures.

The tests found that foam insulation of the present invention has an impact
20 strength of 250 in-lb/in at 70°F and 110 in-lb/in at 250°F .

EXAMPLE 8: Flexural Strength Tests

Flexural strength testing was performed in accordance with ASTM D 790-96a, "Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials." The purpose of this test was to
25 determine if an epoxy syntactic foam of the present invention had sufficient flexibility to withstand the flex stresses it would experience while insulating piping

that was being layed for underwater use. Five samples were tested and were found to have an average flexural strength of 17.2 MPa.

The results indicated that the composite insulation was sufficiently flexible for laying undersea pipelines.

5 EXAMPLE 9: Compressive Strength at Failure Tests

Compressive strength testing was performed in accordance with ASTM D695-96, "Standard Test Method for Compressive Properties of Rigid Plastics." The purpose of the compressive test was to determine the likelihood of crush failure of the syntactic foam insulation at deep depths.

10 Five samples of an epoxy syntactic foam of the present invention were tested. The test results found that the average compressive strength of this foam insulation was 28.3 MPa.

These results indicate that the syntactic foam insulation would not typically crush at depths of less than about 9500 feet.

15 EXAMPLE 10: Hydrostatic Testing

Four pairs of samples of epoxy syntactic foams of the present invention, similar to that described in Example 3 herein, were prepared for testing at 3000 psi. One pair of samples was prepared for hydrostatic testing at 4200 psi. These syntactic foams were of very similar composition with the exception of differences
20 in the density of the substrates upon which the samples were prepared and in the final weight ratio of epoxy resin to curing agent.

The differences in density were produced by varying the amount of air bubbles entrained within the foam samples. The four pairs of foam samples to be tested at 3000 psi had densities of 0.37 g/cc, 0.39 g/cc, 0.44 g/cc and 0.57 g/cc.

25 Regarding the preparation substrates, the 0.39-g/cc and 0.44-g/cc samples were sprayed onto an aluminum sheet using Air-Tech plural spray equipment as described in Example 3. The 0.37-g/cc samples were pumped into an aluminum mold using the Air-Tech plural spray equipment, after mixing to entrain air therein,

without a spray nozzle attached. The 0.57-g/cc samples were pumped into an aluminum mold using the Air-Tech plural spray equipment without mixing to entrain air therein and without a spray nozzle attached.

5 The differences in the final weight ratio of epoxy resin to curing agent in the samples were not significant.

The samples were then cut to form 2-inch by 3-inch by 0.57-to-0.76-inch coupons. Further, in each sample pair, one coupon was coated on five sides, and the other coupon coated on all six sides, with a two-component epoxy primer to mimic uncoated and coated insulation systems.

10 One pair of 0.57 g/cc coupons was prepared for hydrostatic testing at 4200 psi.

The sample pairs were then submitted to National Technical Services (Boxborough, Massachusetts) for hydrostatic testing at 3000 psi or 4200 psi, which correspond to the pressure experienced at depths of about 7100 feet or 10,000 feet, 15 respectively, to determine the moisture absorption of samples at deep sea pressures.

All ten of the tested coupons were labeled, stacked with polypropylene ring spacers between them, and then tied together with a stainless steel wire to prevent movement of the coupons within the steel cylinder hydrostatic test chamber. The coupons were then placed in the test chamber, which was filled with a 5 wt. % 20 solution of salt water and restrained under the salt water by a stainless steel mesh. The test chamber was then sealed and pressurized to 3000 psi or 4200 psi with nitrogen gas.

Previously, each coupon was weighed prior to painting with the two-component epoxy, after painting, and before placement in the test chamber. After 25 hydrostatic testing, for 100 to 400 hours at 3000 psi, or for 100 hours at 4200 psi, each coupon was patted dry with a paper towel and then allowed to air dry at room temperature for an hour prior to weighing.

The hydrostatic test results were as follows:

Sample	Density	Pressure	Time	Weight Percent Gain	
				5-side coated	6-side coated
1	0.37 g/cc	3000 psi	100 hr.	186.8%	91.1%
2	0.39 g/cc	3000 psi	100 hr.	116.3%	112.7%
3	0.44 g/cc	3000 psi	400 hr.	80.0%	81.9%
4	0.57 g/cc	3000 psi	400 hr.	1.2%	1.6%
5	0.57 g/cc	4200 psi	100 hr.	0.7%	0.5%

These results showed that the syntactic foam prepared without entraining air therein (samples 4 and 5) was essentially impermeable to water infiltration as shown by the minor gain of weight. However, the syntactic foam samples containing entrained air (samples 1-3) experienced substantial weight gain due to water infiltration under pressure.

EXAMPLE 11: Thermal Conductivity Test at 3000 psi

Thermal conductivity testing was performed on two specimens of the foam insulation of Example 3 while the specimens were subject to a pressure of about 3000 psi. The purpose of this test was to evaluate the thermal insulating capability of this foam when under pressures higher than that experienced by insulation on deep-submerged underwater pipelines.

The testing was conducted using the method described in ASTM Standard E1225-87 (Reapproved 1993), "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique."

The results of these tests showed that the thermal conductivity of the foam insulation of Example 3 was not affected by the pressurization of the foam insulation to 3000 psi. Thus, the foam insulation was shown to have good insulating properties under deep-submergence pressures.

EXAMPLE 12: Thermal Conductivity Tests at Atmospheric Pressure

Thermal conductivity testing was performed at atmospheric pressure on specimens of the foam insulation of Example 3. The purpose of these tests was to evaluate the thermal insulating capabilities of the foam insulation.

- 5 The testing was conducted using the method described in ASTM Standard E1225-87 (Reapproved 1993), "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique".

Analysis of the results of these tests determined that the thermal conductivity of the specimens was about 0.054 BTU/ft·hr·°F (0.093 W/m·°C), which is sufficient
10 for the tested specimens to be characterized as being good thermal insulators.

EXAMPLE 13: Salt Fog Testing for Corrosion Under Insulation

- Three sections of black carbon steel pipe (6-inch sections with a 1-1/2-inch diameter) were sand blasted to clean their outer surfaces, painted with an inorganic zinc primer and then insulated with 1/2-inch-thick precast and cured sections of an
15 epoxy syntactic foam of the present invention. These sections were adhered to the primed steel pipe using an appropriate high-temperature, corrosion-resistant adhesive previously described herein. In each section, a notch was cut through the insulation down through the primer to the underlying steel. These insulated pipe sections were then subjected to salt fog testing, in accordance with ASTM B117-95,
20 "Standard Practice for Operating Salt (Fog) Apparatus," for 3000 hours, 5000 hours and 6000 hours, respectively.

The results of these tests showed visible corrosion in the notches by 3000 hours, but no corrosion under the insulation even after 6000 hours.

EQUIVALENTS

While this invention has been particularly shown and described with references to preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without
5 departing from the spirit and scope of the invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. An insulated pipe, comprising:
 - a) a metal pipe having an outer surface; and
 - 5 b) an insulation layer covering the outer surface of the metal pipe, the insulation layer including:
 - (i) at least one cured epoxy resin binder, and
 - (ii) hollow microballoons.
2. An insulated pipe of Claim 1, wherein said insulation layer is crush resistant.
- 10 3. An insulated pipe of Claim 1, wherein the microballoons can withstand a pressure of at least 29 MPa without breaking, fracturing or collapsing.
4. An insulated pipe of Claim 1, wherein the microballoons can withstand processing by a medium to high shear mixer without breaking, fracturing or collapsing.
- 15 5. An insulated pipe of Claim 1, wherein the insulation layer further includes at least one type of fiber dispersed therein.
6. An insulated pipe of Claim 5, wherein said fibers include silicon-containing fibers.
7. An insulated pipe of Claim 1, wherein the insulation layer further includes
20 minute amorphous silica particles dispersed therein.
8. An insulated pipe of Claim 7, wherein the amorphous silica particles include fumed silica.

9. An insulated pipe of Claim 1, wherein the insulation layer has a density of about 0.57 g/cm^3 .
10. An insulated pipe of Claim 1, wherein the insulation layer further includes at least one type of gas dispersed therein.
- 5 11. An insulated pipe of Claim 1, further comprising a water-resistant primer layer disposed between the outer surface of the metal pipe and the insulation layer.
12. An insulated pipe of Claim 1, wherein the insulation layer further includes a flexibilizing agent.
- 10 13. The insulated pipe of Claim 1, wherein the insulated pipe is a component of an underwater pipeline at a depth of about 1.8 km or deeper.
14. A mastic used to form a syntactic foam coating on a metal pipe, comprising:
 - a) at least one epoxy resin;
 - b) at least one epoxy curing agent;
 - 15 c) particles of amorphous silica; and
 - d) hollow microballoons.
15. The mastic of Claim 14, wherein the amorphous silica is fumed silica.
16. A mastic of Claim 14, further comprising fibers.
17. A mastic of Claim 16, wherein the fibers include silicon.

18. A method for forming a low-density, crush-resistant syntactic foam insulation layer on a metal pipe, comprising:
- a) forming a liquid epoxy-based mastic including at least one type of epoxy resin and microballoons dispersed therein; and
 - 5 b) applying the liquid mastic onto the exterior surface of a metal pipe to form a mastic coating on said surface, whereupon said mastic coating then cures to form a syntactic foam insulation layer.
19. A method of Claim 18, wherein the liquid mastic is applied onto the exterior surface of a pipeline without rupturing the microballoons.
- 10 20. A method of Claim 19, wherein the liquid mastic is sprayed onto the exterior surface of the metal pipe without rupturing the microballoons.
21. A method of Claim 18, wherein the liquid mastic is sprayed back and forth, depositing a coating having a thickness of at least about 1 cm per spray pass.
22. A method of Claim 21, further comprising the step of mixing the
15 microballoons in the mastic with a medium to high shear mixer.
23. A method of Claim 18, further comprising the step of immersing the insulated metal pipe at underwater depths of about 1.8 km or deeper.
24. A method of Claim 18, further comprising the step of stirring the mastic in a container having a pressure greater than ambient.

25. A method of Claim 18, further comprising the step of mixing a first component and a second component to form the liquid epoxy-based mastic, the first component including an epoxy resin and the second component including a curing agent.
- 5 26. A method of forming an insulated metal pipe comprising the steps of:
- a) casting and curing syntactic foam insulation including epoxy and microballoons; and
 - b) using an adhesive to apply the cast and cured syntactic foam insulation to a substrate.
- 10 27. A method of Claim 26, wherein the substrate is a metal pipe.

INTERNATIONAL SEARCH REPORT

Inter. Natl. Application No

PCT/US 99/09401

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08J9/32 B29C67/20 F16L59/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08J B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 05447 A (CUMING CORP) 4 February 1999 (1999-02-04) claims ----	1-13, 18-24
X	SHELL POLYMERS, vol. 7, no. 3, 1983, pages 80-81, XP002112542 *the whole document* ----	1-13, 18-24
X	WO 94 20286 A (ARNOTT THOMAS CHRISTOPHER) 15 September 1994 (1994-09-15) page 11, line 7 - line 12; claims ----	1-13, 18-24
X	US 5 182 318 A (SAVIN RONALD R) 26 January 1993 (1993-01-26) claims -----	14-17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

18 August 1999

Date of mailing of the international search report

31/08/1999

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/09401

Patent document cited in search report		Publication date	Patent family —member(s)		Publication date
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US 5182318	A	26-01-1993	WO	9410250 A	11-05-1994
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